Exploratory studies on fast pyrolysis oil upgrading

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CHAPTER 1

Introduction

1.1 Introduction

Environmental issues and the security of energy supply have stimulated interest to develop non fossil energy carriers and chemicals. Biomass has been identified as a promising feedstock for these applications. The amount of biomass used for energy generation on a world wide basis was estimated at 30-55 EJ/year (2003) (out of 270-450 EJ/year available) and potentially increases to 100-400 EJ/year in 2030 [1]. As a comparison, the total global primary energy consumption in 2003 was 370-400 EJ/year, of which *ca.* 20-25% was used in the transportation sector. Biomass is abundantly available and CO_2 neutral. Disadvantages are the currently relatively high cost compared to fossil resources, the competition with food and feed and the large area of land required for the production of biomass [2]. Therefore, conversion processes with a high energy yield per hectare are required. A promising conversion technology to meet this requirement is flash pyrolysis.

In the last decade, flash pyrolysis of biomass has gained large attention due to its ability to produce a liquid product with yields up to 80 wt% on dry biomass. The remaining products are char (10-20 %) and combustible gasses (10-30%) [3]. Fast pyrolysis is a medium temperature process (400-500 ^{0}C) in which biomass is rapidly heated (typically less than 2 seconds) in the absence of oxygen

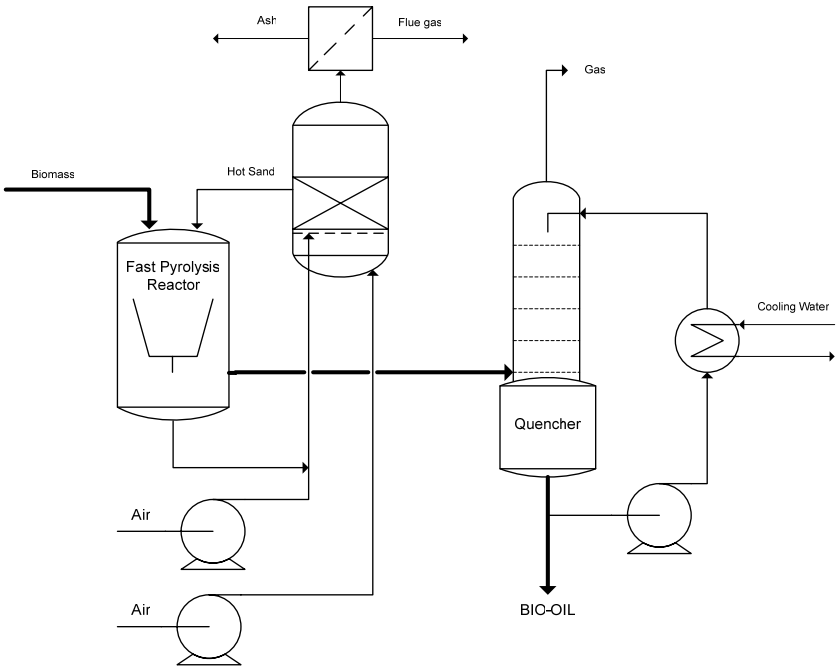


Figure 1-1, Process flow Diagram of BTG's fast pyrolysis process of biomass for bio-oil production. (Courtesy of BTG B.V.) [4]

Developments in fast pyrolysis technology have been impressive and the process is now close to full scale commercialization. For example, the latest two plants being constructed were a 1200 kg/hr unit of BTG/ Genting Sanyen in Malaysia and an 8000 kg/hr Dynamotive Plant in Canada. Several process concepts have been explored, examples are given in Table 1.1.

Table 1-1. Bio-oil technology status

Organization	Country	Technology	Capacity (in kg/h)
BTG/KARA[1]	Netherlands	Rotating Cone	200
ENEL/Ensyn[1]	Italy	Circulating Transported bed	625
University Hamburg[1]	Germany	Fluid bed	50
VTT/Ensyn[1]	Finland	Circulating transported bed	20
Wellman Proc. Eng. Ltd. [1]	UK	Fluid bed	250
BTG/ Genting Sanyen Bhd.[2]	Malaysia	Rotating cone	1200
Dynamotive [3]	Canada	Fluid Bed	8000

Sources: [1)][5]; [2)] [6]; [3)][7]

Flash pyrolysis liquid, also known as bio-oil (henceforth BO), is a dark brown liquid with a pungent odor. The higher heating value is about 16-19 MJ/kg, depending on the water

content. This value is about half of that of crude oil (42 MJ/kg). However, BO contains less ash and is easier to transport than the biomass source. Some important product properties are shown in Table 1.2. The product is rather acidic, contains high amounts of water and bound oxygen and has a relatively high viscosity. Upon storage, the oil tends to phase separate and to solidify.

Table 1-2. Typical properties of wood derived BO [3].

Properties	Typical Value	Unit
Moisture content	15-30	%
pH	2.5	
Specific gravity	1.2	
Elemental analysis, dry basis		
- C	56.4	%
- H	6.2	%
- O (by difference)	37.3	%
- N	0.1	%
- Ash	0.1	%
HHV as produced (25% water content)	16-19	MJ/kg
Viscosity (at 40^{o}C and 25% water)	40-100	cP
Solid (char)	0.5	%

BO contains up to thousand chemical components that may be classified according to functional groups. Typical compound classes in BO are organic acids, aldehydes, ketones, phenolics and alcohols. A detailed composition according to compound classes and a quantification of the major components is shown in Table 1-3.

Although the higher-heating-value (HHV =16-19 MJ/kg) of BO is less than crude oil, BO has shown to be a valuable energy carrier and may be used for important commercial applications like heat and power generation [8-10]. BO has been tested in a 2.5 MWe Orenda Aerospace gas turbine for power generation [11]. BO produced by Red Arrow Products Company was co-fired in a 20 MWe coal station at the Manitowoc power station in Wisconsin. BO produced by BTG has also been co-fired in a 350 MWe power station in Harculo, the Netherlands [11].

Furthermore, BO as well as certain fractions and discrete components, may be used as replacements for fossil based chemicals. For instance, the water fraction is used as a food aroma (liquid smoke). Other emerging areas for BO utilization are the recovery of acetic acid, the use as adhesives [12], fuel enhancers and as fertilizers [13]. However, upgrading of BO is required for applications with have to meet stringent product requirements, like in the area of liquid transportation fuels.

Table 1-3. Compounds identified in various Bio-oils [3]

Compound	Bio-oils [wt%]
Acids	
Formic (methanoic)	0.3-9.1
Acetic (ethanoic)	0.5-12
Propanoic	0.1-1.8
Hydroxyacetic	0.1-0.9
2-Butenoic (crotonic)	-
Butanoic	0.1-0.5
Pentanoic (valeric)	0.1-0.8
2-Me butenoic	-
4-oxypentanoic	0.1-0.4
4-Hydroxypentanoic	
Hexnoic (caproic)	0.1-0.3
Benzoic	0.2-0.3
Heptanoic	0.3
Esters	
Methyl formate	0.1-0.9
Methyl acetate	-
Methyl propionate	-
Butyrolactone	0.1-0.9
Methyl crotonate	-
Methyl n-butyrate	-
Valerolactone	0.2
Angelicalactone	0.1-1.2
Methyl valerate	-
Guaiacols	
2-Methoxy phenol	0.1-1.1
4-Methyl guaiacol	0.1-1.9
Ethyl guaiacol	0.1-0.6
Eugenol	0.1-2.3
Isoeugenol	0.1-7.2
4-Propylguaiacol	0.1-0.4
Acetoguaiacone	0.8
Propioguaiacone	0.8
Syringols	
2,6-DiOMe phenol	0.7-4.8
Methyl syringol	0.1-0.3
4-Ethyl syringol	0.2

Compound	Bio-oils [wt%]
Alcohols	
Methanol	0.4-2.4
Ethanol	0.6-1.4
2-Propene-1-ol	-
Isobutanol	-
3-Methyl-1-butanol	-
Ethylene glycol	0.7-2.0
Ketones	
Acetone	2.8
2-Butenone	-
2-Butanone (MEK)	0.3-0.9
2,3 Butandione	-
Cyclo pentanone	-
2-Pentanone	-
3-Pentanone	-
2-Cyclopentenone	-
2,3-Pentenedione	0.2-0.4
3-Me-2-cyclopentene-2-ol-1-one	0.1-0.6
Me-cyclopentanone	-
2-Hexanone	-
Cyclo hexanone	trace
Methylcyclohexanone	-
2-Et-cyclopentanone	0.2-0.3
Dimethylcyclopentanone	0.3
Trimethylcyclopentenone	0.1-0.5
Trimethylcyclopentanone	0.2-0.4
Furans	
Furans	0.1-0.3
2-Methyl furan	0.1-0.2
2-Furanone	0.1-1.1
Furfural	0.1-1.1
3-Methyl-2(3h)furanone	0.1
Furfural alcohol	0.1-5.2
Furanoic acid	0.4
Methyl furoate	-
5-Methylfurfural	0.1-0.6
5-OH-methyl-2-furfural	0.3-2.2
Dimethyl furan	-

Compound	Bio-oils [wt%]
Aldehydes	
Formaldehyde	0.1-3.3
Acetaldehyde	0.1-8.5
2-Propenal (acrolein)	0.6-0.9
2-butenal	trace
2-Metyl-2-butenal	0.1-0.5
Pentanal	0.5
Ethanedial	0.9-4.6
Phenols	
Phenol	0.1-3.8
2-Methyl phenol	0.1-0.6
3-Methyl phenol	0.1-0.4
4-Methyl phenol	0.1-0.5
2,3 Dimethyl phenol	0.1-0.5
2,4 Dimethyl phenol	0.1-0.3
2,5 Dimethyl phenol	0.2-0.4
2,6 Dimethyl phenol	0.1-0.4
3,5 Dimethyl phenol	-
2-Ethylphenol	0.1-1.3
2,4,6 Trimethyl phenol	0.3
1,2 DiOH benzene	0.1-0.7
1,3 DiOH benzene	0.1-0.3
1,4 DiOH benzene	0.1-1.9
4-Methoxy catechol	0.6
1,2,3 Tri-OH-benzene	0.6
Alkenes	
2-Methyl propene	-
Dimethylcyclopentene	0.7
Alpha-pinene	-
Dipentene	-

Compound	Bio-oils [wt%]
Propyl syringol	0.1-1.5
Syringaldehyde	0.1-1.5
4-Propenylsyringol	0.1-0.3
4-OH-3,5-diOMe pheyl ethanone	0.1-0.3
Sugars	
Levoglucosan	0.4-1.4
Glucose	0.4-1.3
Fructose	0.7-2.9
D-xylose	0.1-1.4
D-Arabinose	0.1
Cellobiosan	0.6-3.2
1,6 Anhydroglucofuranose	3.1

Compound	Bio-oils [wt%]
Misc. Oxyeqnates	
Hydroxyacetaldehyde	0.9-13
Acetol (hydroxyacetone)	0.7-7.4
Methylal	-
Dimethyl acetal	-
Acetal	0.1-0.2
Acetyloxy-2-propanone	0.8
2-OH-3-Me-2-cyclopentene-1-one	0.1-0.5
Methyl cyclopentenolone	0.1-1.9
1-Acetyloxy-2-propanone	0.1
2-Methyl-3-hydroxy-2-pyrone	0.2-0.4
2-Methoxy-4-methylanisole	0.1-0.4
4-OH-3-methoxybenzaldehyde	0.1-1.1
Maltol	-

Considerable efforts have been devoted to fast pyrolysis oil upgrading and involve a large variety of techniques. A clear distinction can be made between *in-situ* upgrading (hydropyrolysis, catalytic flash pyrolysis, etc) and modification of the BO product by a subsequent treatment (post-pyrolysis upgrading). Examples of the latter are *e.g.* hydrotreating and blending with other energy carriers. With these techniques, the conversion of BO to products with properties close to that of conventional liquid transportation fuels comes within reach.

This chapter reviews the upgrading approaches available for BO with the primary objective to obtain energy-carriers with improved product properties. Integrated fuel and chemical strategies are an attractive option to increase the economic attractiveness of BO [14]. Therefore, upgrading processes of BO to obtain valuable chemicals are also included in this overview. The overview does not cover all available literature, only generic technologies supported by relevant examples are provided.

1.2 State of the art for upgrading processes for BO to obtain fuels and chemicals

A large number of processes have been reported to upgrade fast pyrolysis oil to improve its product properties and to extent the range of applications in the field of energy generation and chemical production [10,14-18]. Upgrading technology may be classified as follows: (i) physical and (ii) chemical upgrading. Examples of physical upgrading are blending with

petroleum diesel using surfactants and with additives/solvents, all with the objective to improve the product properties [10,16]. Furthermore, typical separation processes like extraction and distillation are used to recover valuable chemicals [19]. Typical chemical upgrading processes are alcohol treatments using catalysts [20], hydro-deoxygenation and hydro-cracking [21-26].

1.2.1 Physical Upgrading of Bio-oil

In this paragraph, the use of physical, non reactive methods to upgrade pyrolysis oil with the objective to obtain chemicals and energy carriers will be summarized. Examples of non reactive upgrading technologies are extraction, distillation and blending with other liquid energy carriers. An overview of methodology and applications is given in Figure 1.1.

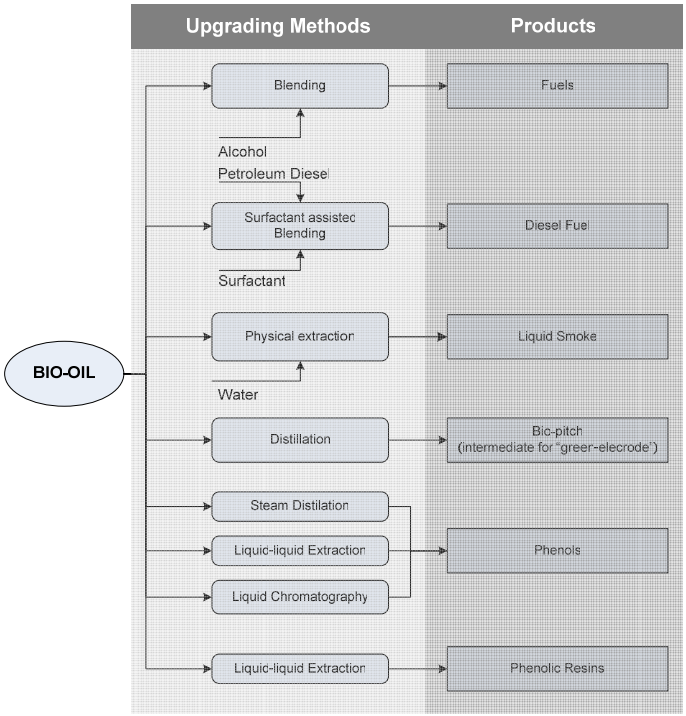


Figure 1-1. Chemicals and fuels from bio-oil by physical upgrading.

1.2.1.1 Non reactive upgrading processes for chemical production

A well known example of a physical upgrading technique to obtain chemicals is dilution of the BO with water to produce liquid smoke [19]. Liquid smoke is a flavoring foodstuff which not only gives the foodstuff a smoke flavor but also leads to the typical darkening of smoked food. The dark color is caused by the reaction of the carbonyl compounds in the liquid smoke with the foodstuff. Currently liquid smoke is made by conventional (slow)

pyrolysis. This leads to relatively low yields of the desired product and a high content of undesirable products like benzo-α-pyrene, a known carcinogen.

Underwood *et al* [19,27] have patented an improved production method for an aqueous liquid smoke solution from BO with high production rates. The method consists of dilution of BO with water to achieve a partial phase separation. With this procedure and by using a fast instead of slow pyrolyis oil, the benzo-α-pyrene concentration in the liquid smoke was less than 1.0 ppb. Furthermore, the product exhibited higher contents of phenolics (flavoring), acids (preservatives) and carbonyls, leading to a much improved browning index. The latter is used as an indicator for the browning performance of liquid smoke. It was shown that hydroxyacetaldehyde and acetol, present in the liquid phase of the BO in large amounts, play an important role in the browning ability of the liquid smoke. As only the aqueous phase of the BO is used for liquid smoke production, the integration of this process with others that utilize the organic phase of BO (*e.g.* as an energy carrier) is very attractive.

The production of biopitch (a viscous organic resin) from BO to substitute fossil pitches in electrodes has been assessed by Rocha *et al* [28]. It was produced by distillation of BO in bench-scale equipment at temperatures of 250-270°C, a heating rate of 2-5 °C/min and pressures ranging between 0.05-0.1 MPa. A 50 wt% yield of biopitch was achieved. The biopitch was mixed with charcoal and thermally modified to obtain electrode material. The electrodes from BO are structurally and chemically different from those obtained from fossil pitch. The oxygen content in biopitch is substantially higher (ca 20 wt%) than in fossil pitch (less than 2 wt%). Product properties like resistivity, Young's modulus, rupture-strength, density and porosity were determined and were shown to be comparable to standard materials made from fossil resources.

Isolation of phenolics, either pure or a as a mixture of compounds, has been comprehensively investigated using a variety of separation techniques. Pakdel and co-workers [18,29] showed that BO derived phenolics have a wide window of applications, for example in leather tanning, in dyes, in thermal insulating materials and as food additives [29].

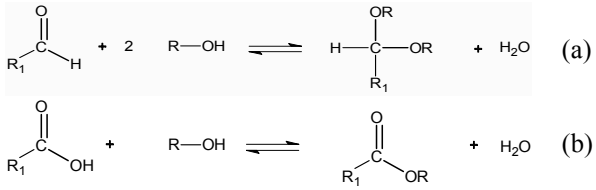
Liquid-liquid extraction [18], steam distillation [29] and liquid phase chromatography have been used for the isolation of phenolics [30]. Amen-Chen *et al* have investigated the isolation of phenolics from pyrolysis tar with the objective of recovering valuable pure phenols, *e.g.* phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol [18]. The procedure consists of four steps: (1) dissolving the wood tar-derived oil (containing the desired phenols) in ethyl acetate; (2) addition of an aqueous alkaline solution to extract phenols by converting

them into water-soluble phenolate ions; (3) regeneration of phenols by acidification of the aqueous layer with sulfuric acid; and (4) recovery of a phenolic-rich fraction by ethyl acetate extraction of the acidic aqueous layer. Removal of phenols was more efficient under highly alkaline conditions.

Murwanashyaka *et al* investigated the potential of steam distillation to recover syringol (2,6-dimethoxyphenol) from BO obtained from wood [29]. The oil was subjected to a steam distillation and the recovery of phenolics was studied at various steam to BO ratios. 14.9% wt of a volatile pyrolysis oil fraction was recovered at a steam-to-BO ratio of 27. GC/MS analysis of the (acetylated) distillate revealed 21.3% by wt. of phenolic compounds. The distillate was further fractionated under vacuum and *ca.* 16 sub-fractions were recovered. The steam-distilled fractions were found to be chemically and thermally stable when subjected to further purification processes. The (syringol)-rich fraction was separated and purified to obtain syringol with a purity of 92.3%.

1.2.1.2 BO upgrading to liquid energy carriers by physical processing

BO blends with alcohols have been investigated to improve the product properties and to make the product suitable for use in stationary and in-stationary internal combustion engines [20]. Methanol was found to be the most effective alcohol among others tested (ethanol and iso-propanol). The products showed higher homogeneity, lower viscosity, lower density and lower flash points and considerably higher HHV's (high heating value). The reduction in the viscosity was ascribed to a stabilizing effect of the alcohols on the water-insoluble high molecular weight lignin-derived fraction. Alcohol addition also had a positive effect on storage stability and the rate of molecular weight built-up during aging was lowered. Low concentrations of alcohols ($\leq$5 wt %) prevented BO from aging by a few months, while higher alcohol content (up to 10 wt %) retarded aging by almost a year. The most interesting features offered by this approach are its simplicity, low cost of the alcohol and the beneficial effects on the product properties. Hence, alcohol addition has been suggested to be the most practical approach to upgrade BO [31]. From a chemical point of view, it was found that both ester and acetal formation occurs (Scheme 1.1). This is also an indication that aldehydes and/or organic acids are responsible for the relatively poor storage stability of BO. Although product properties were improved, no indication was given whether the product is suitable as a transportation fuel.



Scheme 1-1. Reactions taking place during alcohol addition.

Ikura *et al*. studied BO upgrading by blending it with diesel fuel in the presence of surfactants. The latter is essential because BO is immiscible with petroleum diesel [16]. Two commercially available surfactants (Hypermer B246SF and Hypermer 2234) were used. Both were applies in equal amounts and diluted with methanol in a 5:2 methanol to surfactant ratio. The relationship between process conditions (*e.g*. BO and surfactant concentration, residence time, power input, and temperature), emulsion stability and processing cost were determined. The emulsion stability was determined by measuring the stratification rate. Dominant parameters affecting the emulsion stability were the BO concentration, surfactants concentration and power input. The formation of stable emulsions required surfactant concentrations ranging from 0.8 to 1.5 wt%. The cetane number of the emulsions decreased by 4 points for each 10%-wt increase in BO concentration. Emulsion viscosities, particularly in the 10–20% bio-oil concentration range, are substantially lower than the viscosity of bio-oil itself, making these products very easy to handle. The corrosiveness of the emulsions is about half of the corrosiveness of pure BO. One of the drawbacks of this process is the high cost for producing stable emulsions (handling costs including the surfactant cost). However, the cost could be reduced to 50% when introducing a cheap surfactant from ricinoleic acid for BO-Diesel blends.

1.2.2 Chemical upgrading of Bio-oil

A wide range of valuable products (*i.e*. chemicals, transportation fuels and fuels for heat and power generation) is accessible by means of chemical upgrading. In this paragraph upgrading processes involving a chemical reaction with or without the presence of catalysts are discussed.

1.2.2.1 Production of valuable chemicals from BO using chemical upgrading

H_2 generation from BO by steam reforming is extensively investigated [32-34] (Scheme 1-2). As hydrogen is expected to become an important future energy carrier, this route could become a promising way to supply hydrogen from biomass. Rioche *et al* studied the use of noble metal catalysts for reforming BO model compounds (acetic acid, acetone, ethanol and phenol) and actual BO. Temperatures between 650-950°C were employed to reform model compounds over Pt, Pd and Rh catalysts supported on alumina and ceria–zirconia. The following order in catalyst activity was observed: 1% Rh-$CeZrO_2$ > 1% Pt-$CeZrO_2$ ~ 1% Rh-Al_2O_3 > 1% Pd-$CeZrO_2$ > 1% Pt-Al_2O_3 > 1% Pd-Al_2O_3. The use of ceria-zirconia supports led to higher H_2 yields compared to alumina supports.

$$\underset{\text{Bio-Oil}}{\text{-(CH}_2\text{O)-}} + \text{(x-1) . H}_2\text{O} \xrightarrow[> 800^{o}\text{C}]{} \text{CO}_x + \text{x . H}_2$$

Scheme 1-2. Hydrogen production by steam reforming of BO

Steam reforming of crude BO from fast pyrolysis of beech wood using the above mentioned ceria–zirconia supported catalysts gave similar yields of hydrogen and CO_x as found for the model compounds. A hydrogen yield above 50% was maintained over a 9 h reaction time using a 1% Pt-$CeZrO_2$ catalyst and operating at a steam to carbon ratio of 5.0. The use of auto thermal conditions (by co-feeding oxygen) reduced the extent of carbon formation, but led to a significant reduction in hydrogen yield and accelerated catalyst deactivation. Further feasibility studies are needed to assess the economic attractiveness of this route. Finding a cheap and stable catalyst will be a challenging aspect.

A method for producing calcium salts of organic acids (Bio-Lime™) has been developed by Oehr *et al* [35]. The calcium salts, such as calcium acetate, calcium formate or calcium propionate, were obtained from the aqueous phase of phase separated pyrolysis oil. Distillation of this fraction afforded a distillate rich in organic acids as well as the corresponding esters and formaldehyde. The distillate was neutralized with a basic calcium salt (*e.g.* CaO or lime) to produce insoluble calcium salts of the organic acids. The water and volatile organic components were removed by evaporation leaving a solid residue consisting of calcium acetate, formate and propionate. An illustrative description of the process is shown in Figure 1-2.

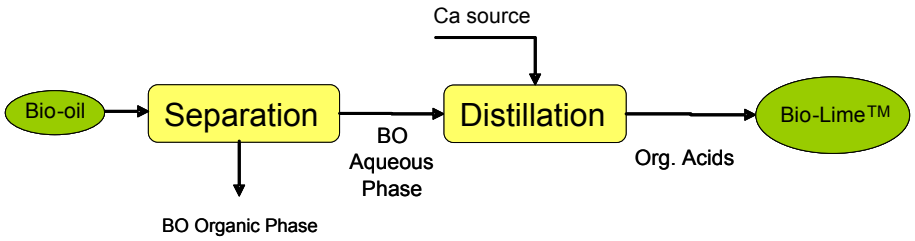


Figure 1-2. BIO-LIME™ process to produce calcium salts of organic acids

The BioLime products are applied to remove contaminants (*e.g.* SO_2 or NO_x) from flue gas. For example, Steciak *et al* shows that calcium magnesium acetate is effective for both NO_x and SO_x removal from a flue gas of a coal fired power plant [36]. Zhang *et al* describes the use of calcium acetate solutions to impregnate coal prior to combustion to reduce sulphur emissions of coal fired power plants [37].

1.2.2.2 Production of energy carriers from BO using chemical upgrading

The production of liquid BO derived products with improved product properties for use in power and heat generation and in stationary and in-stationary internal combustion engines has been investigated by various authors. Among them, hydrotreating of BO for the production of hydrocarbon like products was given most attention [38-60]. The reaction, also known as a hydrodeoxygenation (HDO) reaction, is schematically represented in Scheme 1-3. The reaction has strong analogies with typical refinery hydrogenations like hydrodesulphurization (HDS) and hydrodenitrification (HDN). In general, most of the hydrodeoxygenation studies have been performed using existing hydrodesulphurization (HDS) catalysts (NiMo and CoMo on suitable carriers). Such catalyst need activation using a suitable sulphur source and this is a major drawback when using nearly sulphur-free resources like BO.

$$-(CH_2O)- + H_2 \rightarrow -(CH_2)- + H_2O$$

Scheme 1-3. Simplified schematic representation of hydrodeoxygenation (HDO) of bio-oil

The first studies on the hydrotreatment of pyrolitic oils with the objective to reduce the oxygen content were performed by Elliot *et al* [53,61]. The reaction was performed in a bench scale reactor configuration consisting of two fixed bed reactors operated at 21 MPa hydrogen

pressure (Figure 1-3). Both reactors were operated in a down-flow (trickle bed) operation. The first reactor was operated at low-temperature (150-200°C) and is regarded as the stabilization reactor. The second was operated at much higher temperatures (300-400°C) and here the desired hydrodeoxygenation reaction takes place. NiMo and CoMo on γ-alumina were used as the hydrotreating catalysts. The deoxygenation rate was found to be dependent on the liquid hourly spaced velocity (LHSV) and complete deoxygenation could be achieved at a LHSV of *ca.* 0.1 hr^{-1}. The product properties of the hydrotreated oil like viscosity and density were determined and shown to be a function of the residual oxygen content. Both properties were lowered at higher product deoxygenation levels. Techno-economical evaluations have indicated that the costs of BO, hydrogen and the capital cost are the major cost factors. Surprisingly, catalyst costs were not included, although it has been demonstrated by many authors that catalyst deactivation for HDO processing may be severe, leading to high variable catalyst costs.

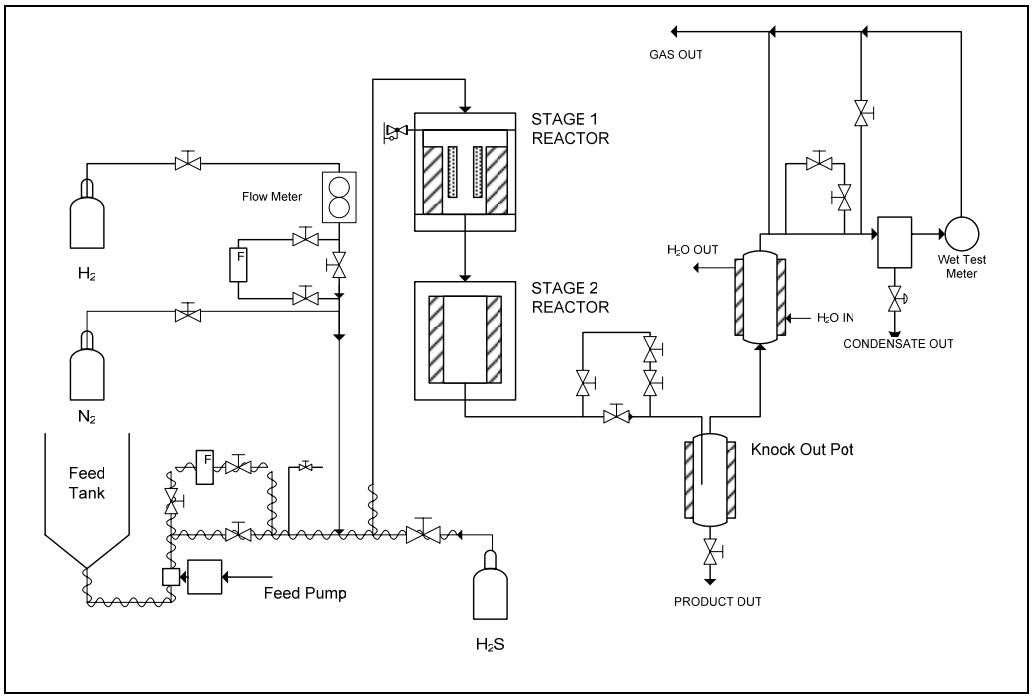


Figure 1-3. A schematic representation of the bench-scale, down flow continuous-feed, fixed-bed reactor system for HDO of BO [61]

A comprehensive kinetic study on BO hydrotreating over a wide range of operating conditions (350-450°C, 50-100 bar, and weight hourly space velocities between 0.5-3.0 hr^{-1}) was performed in a trickle bed reactor using $Pt/Al_2O_3/SiO_2$ and conventional

hydrodesulphurization catalysts like sulfided $CoMo/A1_2O_3$, $Ni\text{-}W/\gamma\text{-}A1_2O_3$ and $Ni\text{-}Mo/\gamma\text{-}A1_2O_3$ [44]. Two models, one for overall oxygen removal and the other for the compositional changes in the hydrotreated oil, were developed. The amount of oxygen in the product was used as the base for the modeling.

Baldauf *et al*. studied [62] the hydrotreatment of BO both in a thermal and catalytic mode (Figure 3). Thermal hydrotreatment resulted in 70-80 %wt reductions in oxygen content in the final product whereas > 90% deoxygenation was achieved when using catalysts. Depending on the severity and the water content of the feedstock, a product yield of 30-50 % could be achieved. The product was fractionated by distillation and it was shown that the product properties of the heavy fraction are close to those of a fluid catalytic cracking (FCC) feedstock. The light fraction had properties close to that of gasoline.

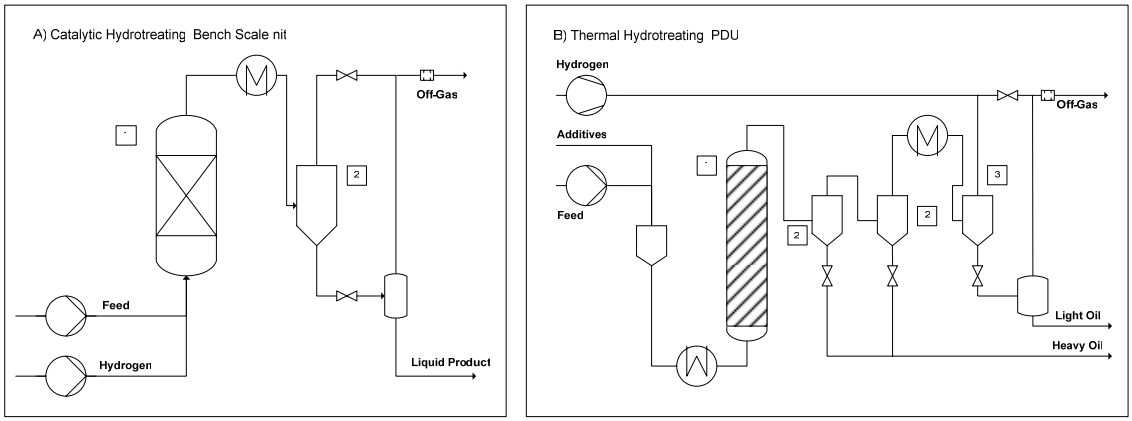


Figure 1-4. Experimental set-up used by Samolada *et al*. [62]. (a) Catalytic hydrotreating bench scale unit (1: Fixed bed reactor; 2: separator). (b) Thermal hydrotreating process development unit (PDU) (1: reactor; 2: hot separator; 3: cold separator)

Hydrocracking of BO by HZSM-5 has been investigated by Sharma and co-workers [48,63-67] with the objective to increase the amount of aromatic hydrocarbons. A reactor system consisting of fixed-bed micro-reactors was used and operated at atmospheric pressure and temperatures between 370 and 410°C. The oil was co-fed with diluents such as tetralin, steam and methanol. A certain amount of gas was produced, usually less than 5% wt on intake. At higher temperatures, over 30% wt of the oil was converted to coke. The liquid products separated into an organic and aqueous phase. The organic phase was distilled under vacuum (1.3 tor at 200°C) for 30 min. The upgraded product contained large amounts of benzene,

toluene, xylene and other aromatic hydrocarbons. Furthermore, phenolics were present, however, at a level much lower than in the original BO. The concentration of phenolics was a function of the type of diluent used and the hydro-cracking temperature. The phenol concentration increased with the following order of diluent: tetralin >> steam ~ methanol; and decreased with increasing temperature.

Table 1-2. Summary of BO upgrading methodology for chemicals and fuel production.

No	References	Product Category	Process category	Application	Approach
1	[20,68]	Power	P[1]	Gas turbine	Alcohol addition
2	[63,66,67,69,70]	Fuel	C[1]	Transportation fuel	2 stages Hydro-cracking by HZSM-5, 350-450^{o}C
3	[71]	Fuel	C	Transportation Fuel/ Gasoline blending	2 stages Hydro-treating using HDS Cat. 250-450^{o}C, 2000 psig.
4	[10,16]	Power	P	Stationary Diesel Engine fuel	Emulsification using surfactants.
5	[62]	Fuel	C	Transportation Fuel	Hydro-treating-FCC dual treatment
6	[72]	Fuel Chemical	C	Transportation Fuel/Power	Alcoholysis by reactive adsorption using molecular sieve 3A
7	[32,73]	Chemical Fuel	C	H_2	Steam reforming for H_2 production using Ni-based catalyst or noble metal catalyst
8	[74-76]	Chemical	C	Levoglucosane	Recovery by extraction.
9	[35]	Chemical	P	Calcium salt (road de-icers) (Calcium formate, C. acetate, propionate)	Distillation of aqueous BO to obtained acids – pH adjustment of the distillate using alkaline followed by water evaporation.
10	[77]	Chemical	C	Resins and Adhesives Phenol Formaldehyde	Series of liquid-liquid extraction of BO using solvents like ethyl acetate followed by sequential back-extraction with water and bicarbonate solution.
11	[28]	Chemical	C	Bio-pitch, electrode manufacturing	Bio-oil-charcoal distillation in bench scale. Application as a binder in bio-electrode.
12	[19]	Chemical	P	Liquid smoke	Water separation to reduce benzyl-α-pyrene to < 1 ppb
13	[29]	Chemical	P	Syringol	Syringol (92% yield) obtained from vacuum PO by steam distillation
14	[18]	Chemical	P	Phenol & Phenolics	Tar conversion to light oil. Phenolic compounds were further separated from the oil by liquid-liquid extraction using alkali and organic solvents.
15	[78]	Chemical	C	Syngas	Bio-oil conversion to gas was 83 wt %, whereas gas production was 45 L/100 g of bio-oil at 800^{o}C and a constant nitrogen flow rate of 30 mL/min.
16	[79,80]	Chemical	C	Bio-Lime^{TM}	Acidic pyrolysis oil is neutralized by basic alkaline earth metal compounds. Resulting metal carboxylates are used for flue gas treatment.

Note: P: Physical Upgrading, C; Chemical Upgrading

1.3 Thesis Overview

This thesis describes the results of exploratory experimental studies on the upgrading of fast pyrolysis oil. An overview of the research is given in Scheme 1.5. The major incentive was to identify novel upgrading processes to improve the product properties and extent the use of BO as an energy carrier. The first chapter (***Chapter 2***) describes an experimental study on catalytic partial hydrodeoxygenation (HDO) of BO, with the primary objective to increase the energetic value of the oil by removing bound oxygen in the form of water. The process was carried out in two distinct stages, a first stage at relatively low temperatures (250-300^{o}C), aimed to stabilize the BO and a second stage at higher temperatures (300-400^{o}C) to de-oxygenate the intermediate product. Different types of catalysts were screened, ranging from conventional sulfided catalysts used in the HDS process (*i.e.* $NiMo/Al_2O_3$, $CoMo/Al_2O_3$) to novel non-sulfided catalyst based on noble metal catalysts (*i.e.* Ru/Al_2O_3). Operating conditions were optimized to obtain the highest yield of a hydrocarbon like liquid product. The amounts and composition of the various reaction products (gas, organic liquid, aqueous liquid and solid char) were determined to allow determination of the overall mass balance.

Chapter 3 & 4 describe experimental studies on the mild-hydrogenation (40-45 bar, 30-90^{o}C) of various BO fractions using homogeneous ruthenium catalysts. A biphasic, liquid-liquid approach was selected, and tuned in such a way that the homogeneous catalyst was poorly or insoluble in the BO fraction to be hydrogenated. In this way, catalyst recovery of the homogeneous catalyst is facilitated, allowing high catalyst turnover numbers. ***Chapter 3*** describes the biphasic hydrogenation of a BO fraction obtained by a dichloromethane extraction of pure BO in a dichloromethane-water system using a homogeneous water soluble Ru/tri-phenylphospine-tris-sulphonate (Ru-TPPTS) catalyst. Initially, the hydrogenation of model compounds for the dichloromethane fraction of BO, notably phenolics like vanillin, acetoguaiacone, iso-eugenol was investigated in water-dichloromethane mixtures. Hydrogenations were performed in a batch reactor operated at mild operating conditions (45 bar, 40-70^{o}C). The effects of process parameters (*e.g.* temperature, NaI addition, solvents, and pH of aqueous phase) were determined for vanillin and quantified by a kinetic study. Finally, the BO fraction obtained by dichloromethane extraction was also hydrogenated in a biphasic system of water and dichloromethane. Analyses indicate that the oxygen content is lowered substantially and that particularly the amount of reactive aldehydes is reduced considerably. ***Chapter 4*** discusses a similar approach, however, in this case the water-soluble fraction of BO is hydrogenated in a biphasic system using a water insoluble homogeneous Ru-catalyst (Ru/tri-

phenylphospine, Ru-TPP). To gain insights in the potential of this catalyst system, initial experiments were conducted with representative, water soluble model compounds like hydroxyacetaldehyde and acetol. The reaction was performed in a batch reactor operated at mild operating conditions (20-40 bar, 50-90^{o}C). The effects of process parameters (*e.g.* temperature, initial H_2 pressure, and initial substrate concentration) were investigated and for acetol quantified using a kinetic model. Finally, the hydrogenation of the BO water-soluble fraction using the biphasic system at optimized conditions was reported.

Chapter 5 discusses BO upgrading by means of an alcohol treatment. For this purpose, the concept of reactive distillation was employed. The BO is treated with a high boiling alcohol in the presence of an acid catalyst at mild conditions. When employing this procedure, water is produced by reactions of the alcohol with organic acids and aldehydes in the BO. By continuous removal of water, the desired reactions are driven to completion, leading to improved product properties. Variables like the type of alcohol (n-butanol, ethylene glycol, 2-ethyl-hexyl-alcohol) and the type of acid (liquid- and solid acids) were explored. The product properties of the resulting upgraded pyrolysis oil (kinematics viscosity, water content, pH, and heating value) and the optimum conditions were determined.

Organic acid recovery and particularly acetic acid from BO by employing reactive extraction using a suitable amine is discussed in ***Chapter 6***. The effect of process variables on the optimum conditions was determined.

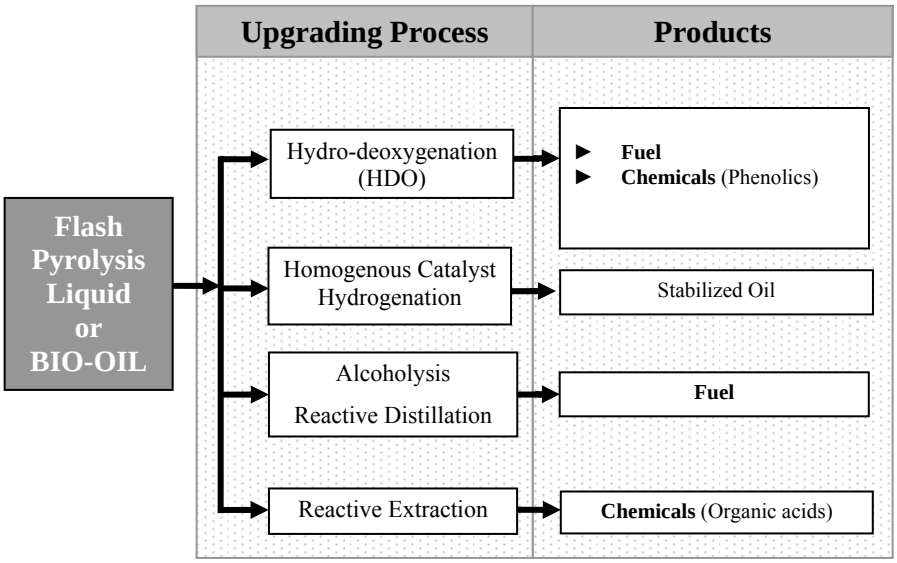


Figure 1-5. Overview of research activities described in this thesis.

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